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Abstract

The reduction of solutions of carbon dioxide (saturated at the room temperature in organic polar solvents such as acetonitrile, AN, or N,N-dimethylfomamide, DMF, containing tetraalkylammonium salts TAAX) was achieved at smooth silver electrodes. Under these conditions, reduction steps were obtained beyond -1.7 V vs Ag / AgCl with exact potentials depending on the size of TAA^+ cations. An unexpected behaviour is noticeable with tetramethylammonium salts (TMA^+X^-) leading to a progressive electrode inhibition upon scans or fixed potential electrolysis at E < -2V. These results are in agreement with the formation of a thick layer of the form {Ag-CO_2^-,TMA^+} strongly sensitive to di-oxygen, water, organic π-acceptors; this layer is considered as a reducing reagent of low chemical stability and can be oxidized before silver. Placed under pure argon atmosphere, the layer decomposes – presumably by instability of TMA^+ in reducing media that permits trapping of large superficial amounts of CO_2 in the material supposing the formation of multi-layers of CO_2 (up to 5×10^{-6} mol cm^{-2}). These novel {silver-CO_2} materials could be seen as dual catalytic-electrophilic electrodes.

Key-words: Silver electrodes; modified electrodes; cathodic carboxylation; Ag-CO_2 dual materials.

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1. Introduction

Undoubtedly, electrochemistry is a very valuable method for insertion of free radicals and ions inside carbon and metallic matrixes. This is an interesting way for creating new interfaces, permitting creation of new catalytic electrodes both within the anodic and cathodic ranges. Among wide possibilities of transforming materials (especially carbons and graphites), one may find in a recent literature works that quoted reactivity of gold [1] and

mercury via tetraalkylammonium (TAA^+) amalgams [2], of platinum and palladium by insertion of salts or/cations within the cathodic range [3]. Still in the field of the insertion of TAA^+ cations, their cathodic reactivity with post-transition metals (antimony, tin, lead) deserves being quoted [4]. In most of cases, such reaction can be considered as the formation of new reducing reagents [5] and should be carried out in an inert atmosphere.

Silver is presently considered as a fascinating metal for its catalytic properties especially in the domain of the scission of carbon-halogen bonds [6,7], and despite its perspective capacities to act as a reducing entity, attempts to modify surfaces or to insert ions into Ag matrixes do not presently appear to have been achieved.

The present contribution concerns small electroactive molecules that can act as vectors to diffuse into metals under their reduced or oxidized form(s) and then inducing the paired insertion of the counter-ion of supporting electrolyte. The case of carbon dioxide is questionable because its reduction potential appears very depending on the electrode material and the electrolyte: obviously, it possesses a strong capability to provoke catalyses and react with cathode materials; glassy carbon [8], graphite [9], or showing specific capacities for catalyzing couplings (e.g. formation of oxalate on lead [10]).

For the first time, the reduction of CO_2 was performed at smooth silver in the presence of TAAX salts in polar aprotic solvents. The great novelty of this approach is that it allowed to disclose that a reduced form of CO_2 (presumably, the anion radical), *exclusively* when combined with TMA^+, may react with silver leading to a large insertion into the electrode matrix until a total surface inhibition, which is manifested by the drop of conduction in the modified metal interface. The insertion product is considered as a reducing reagent. Moreover, a specific oxidation step (that removes the inhibition) was detected, and the reactivity of silver towards carbon dioxide insertion could be proved by change of its pristine structure. Hereafter, is described a first approach concerning CO_2 that quite certainly deserves further extended refinements and can certainly be applied (after exploratory works guided by the present study) to the unexpected carboxylation of a large series of solid materials currently used in electrochemistry.

2. Experimental section

2.1. Salts and solvents

In the present work, 0.1 M solutions of tetramethylammonium, tetraethylammonium, tetra-*n*-butylammonium tetrafluoroborates ($TMABF_4$, TEABF4, and $TBABF_)$ and tetra-*n*-hexyliodide (THAI) in dimethylformamide (DMF) and acetonitrile (AN) were used. Salts and solvents were purchased from Aldrich (quality for syntheses). It is worth mentioning that the procedures given hereafter do not require extremely dry solutions so the solvents were used as

received (water content >800 ppm). For excluding oxygen, all electrochemical experiments were performed under inert atmosphere bubbling argon through the solution. Alternatively, corresponding to the aim of the study, liquid electrolytes were saturated with CO_2 (bubbling for 5 min at room temperature) purchased at Air Liquide.

The reported potentials are all referred to aqueous $Ag/AgCl/KCl_{sat}$ electrode. The electrochemical instrumentation has been previously described [4,5].

2.2. Working electrodes

All silver and glassy carbon (GC) electrodes used in voltammetry had an apparent surface area of 0.8 mm^2. Before using silver and glassy carbon electrode, their surfaces were carefully polished with silicon carbide paper (Struers 500 and 1200) or with Norton polishing paper (type 02 and 03) and rinsed with water, then alcohol and at last with acetone. After recurrent scans or fixed potential electrolyses, silver electrodes were eventually sonicated for two minutes. Finally, before analysis, the electrodes were dried with a hot air flow during about 30 s. Coulometry measurements and electrolyses reported in this work were carried out using three-electrode cells with a total catholyte volume of about 5 mL.

2.3. Organic materials

All organic compounds used for testing silver materials modified by insertion of CO_2 were purchased from Merk and Aldrich.

3. Experimental results

3.1. Experimental evidence of a large carbon dioxide insertion in silver bulk

At first sight, the procedure described in this contribution may appear to the reader totally unexpected. The simultaneous blend of silver metal on the one hand, and a moderate pressure of CO_2 when using an M^+X^- (not too bulky M^+ and anodically stable X^-) electrolyte on the other hand, meeting in a confined reducing space at $E < -1.8$ V may produce a strongly inhibiting organometallic species under specific conditions. More specifically, as featured in Scheme 1, the electrochemical technique may provide a very easy way to form an organometallic entity (proposed to be written as {Ag-CO_2-M}). The experiments described hereafter used essentially solutions of tetramethylammonium tetrafluoroborate (TMA^+ BF_4^-) in DMF saturated in CO_2 (room temperature), considered as a catholyte in which a smooth Ag electrode was plunged. Fixed potential electrolyses at ≤1.8 V led to a quite fast inhibition of the electrode surface until very small current densities are obtained. Voltammetry (Figure 1,

curves A) permits to disclose the progressive decay of the electron exchange that suggests the formation of a thick layer of {Ag-CO_2-M} of weak conductivity. Resting the covered electrode at 0 V under the flow of argon permits to replace CO_2 atmosphere inside the cell, however silver electrode still reacts with CO_2 (Figure 1, B), suggesting the Ag matrix still contains quite large amounts of carbon dioxide really inserted into the metal.

Figure 1 (curves C) illustrates the peculiar action of TMA^+ in the insertion process. Bulkier TAA^+ do not favour the CO_2 electro-activity, neither its insertion into silver. Na^+ (associated to BF_4^-) may be used as well for insertion and supports the importance of the insertion rate in this reaction. A similar process can be achieved in ACN.

MEB analyses do confirm the presence of amorphous or crystalline deposits on the Ag surface (Figure 1, slides D).

3.2. Evaluation of thickness of the inhibiting Ag-CO_2 layer

Assuming the inhibitor coverage process to obey a one-electron reaction (1), as proposed in Scheme 1, the main and sharp peak (**I**) (curve A in Figure 1) may account for the progressive formation of an organometallic species propagating from the surface to the bulk. It is obviously quite thick already at the first scan: $\Gamma_1 = 2.4\times10^{-6}$ mol cm^{-2}. Further recurrent scans provoke a regular decay of the peak current until a quasi absence of response between -1.5 V and -2.0 V after 10 to 12 scans that supposes a progressive filling of the metal. Under the conditions of Figure 1 (scan rate: 50 mV s^{-1}), a quasi total inhibition –depending of the scan rate– is observed for 10^{-5} mol cm^{-2}. Alternatively, fixed potential electrolyses achieved at -2.2 V until a final current density of 5 µA mm^{-2} permitted obtaining the reductions implying $> 10^{-6}$ mol cm^{-2}. Therefore, this method would enable formation of a large multilayer system (roughly more than 10^4 layers) and one might then admit that organometallic diffusion inside the silver bulk occurs upon short reaction times (< 3 min).

3.3. Voltammetric analysis of the {Ag-CO_2-TMA} multi-layer

Once the organo-silver layer is formed (3 successive steps (**I**), total charge: 3.1×10^{-7} mol cm^{-2}) as discussed in § 3.1, its anodic oxidation was achieved as pictured in Figure 2, curves A. Thus, after the insertion of CO_2 in the course of the forward scan, a reverse scan up to + 0.7 V permits to observe an anodic step (**II**) (E_{pII} = 0.36 V, charge: 2.9×10^{-7} mol cm^{-2}) well different of that of Ag metal. Within this potential interval, the anodic oxidation of Ag does not appear consecutively to the inhibiting deposit. It is expected that step (**II**) would correspond to the anodic oxidation of {Ag-CO_2-TMA} (reaction (2)) followed by the decomposition according to reaction (3), presumably liberating CO_2 and Ag^+ particles still

dissociated from the silver mass. In the course of second cathodic scan, one observes another bell-shaped reduction step (**III**) (E_{pIII}= -0.38 V, charge: 3.0×10^{-7} mol cm^{-2}) assigned to the reduction of the organo-metallic layer cation or that of Ag^+ that was shown to be coupled to step **II**. One may notice that charge values relative to steps **I, II,** and **III** are particularly coherent. Also, the experiments achieved in comparable conditions with Pt, Pd, and Au exhibit only two steps **I** and **II** (no corrosion of the host metal). In all cases, surface analyses of metals after carboxylation processes exhibit attachment of carboxylic groups. There are also some evidences that carbon dioxide partly remains in silver after oxidation (reaction 3) and a total regeneration of the gold electrode for further voltammetric analyses require a stay in oven (60 °C) for a few minutes.

3.4. About chemistry of {Ag-CO_2-TMA}

This complex does not appear to be particularly stable. It is sensitive to air (dioxygen), moisture, and the presence of organic acceptors. For example, as depicted in Figure 2 B, the addition of a primary alkyl iodide RI, to the cell with the charged carboxylated silver electrode (voltammetric response in black) led to a sudden decay in CO_2 concentration at the interface (perceived at a maximum of current in red) identical to the first scan during the charge. At the same time, the reduction current corresponding to the catalytic cleavage of RI ($E_p \approx$ -0.9 V) is small. For comparison, a smooth silver electrode (Figure 2 B) led to a much larger reduction step of RI (**V**). Also, the use of "catalytic-carboxylating" electrodes that combine catalysis by Ag and the electrophilic properties of inserted CO_2 permitted to realise carboxylation of unsaturated hydrocarbons. Finally, peared carboxylation reactions using Ag transients in very thin deposits were successfully accomplished onto graphites and graphenes.

4. Conclusion

Here considered as a small-size electroactive molecule, $CO_{2\ (gas)}$ may be successfully inserted into silver under specific conditions principally related to the nature of polar organic solvent and the size of the electrolyte cation. The metal is not only carboxylated in surface (small electricity amounts), but also –and considerably– in the Ag bulk. These preliminary results suggest that the insertion is reversible and may be easily anodically (E < 1.0 V) released; such CO_2-charged electrodes can then be considered as a convenient source of CO_2 for carboxylation reactions with adapted probes (field of micro-electrochemistry). It is interesting to notice that the cleavage of the silver-CO_2 bond reported in this preliminary work is in a certain manner quite similar to the non-Kolbe reaction at carbons [9]. Finally, this reaction could be successfully extended to a large series of metals, in particular Au and Pt.

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Figure captions

Figure 1

Insertion of CO_2 into silver.

A) Voltammetry of saturated solution of CO_2 in DMF at a stationary silver electrode (area: 0.8 mm^2). Electrolyte $TMABF_4$. Scan rate: 100 mV s^{-1}. Decay of the peak current after 9 scans. For comparison: B) voltammetry of the same electrode (without contact with air) after an *in situ* replacement of CO_2 by argon.
C) Voltammetry of CO_2 at silver electrode in DMF in the presence of different electrolytes. Scan rates: 50 mV s^{-1}. TMA^+ (black), THA^+ (green), and TBA^+ (red).
D) MEB analysis of an Ag pristine surface after electrolysis at -2.2 V in the presence of CO_2. Amount of electricity: 1.5 C cm^{-2}.

Figure 2

Voltammetry of the cathodic deposit obtained at Ag in the presence of CO_2 and TMA^+.
A) After formation of the deposit (according to (**I**)), the oxidation of the silver complex (**II**), scan inversion from + 0.7 V. The cathodic step (**III**), assigned to the reduction of Ag^+ arising from the anodic degradation of {Ag-CO_2-TMA}. For comparison, the electrochemical response of the bare silver surface is shown in red. Scan rate: 50 mV s^{-1}.
B) Deposit of the silver complex (black) prior to adding 1-iodohexane (7 mmol L^{-1}). The C-I cleavage step (V) is very small presumably because the Ag-CO_2 complex reduces the RI compound (red) while a few scans entirely restore the coverage. For comparison, the reduction of the RI at smooth Ag (blue) is given.

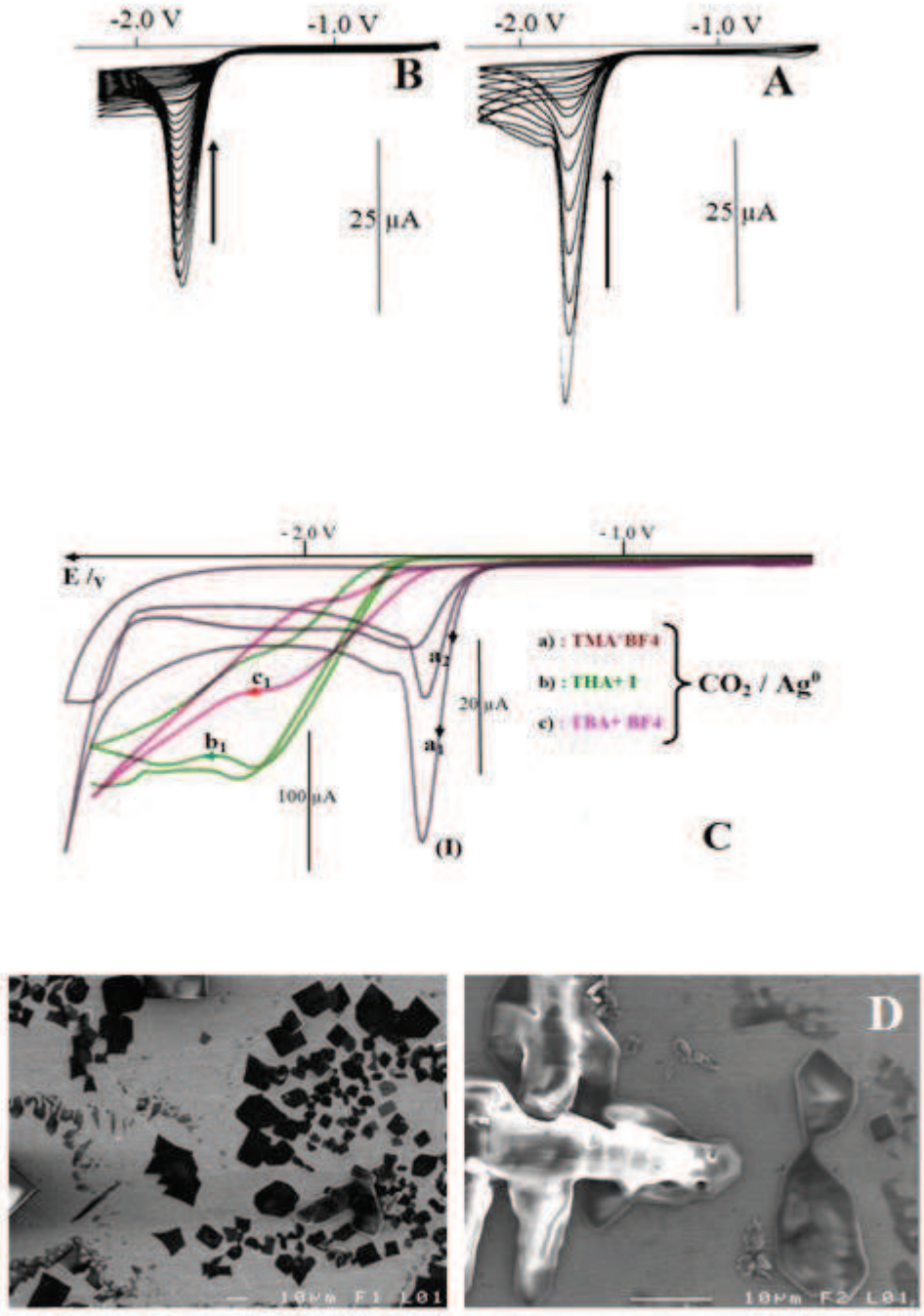


Figure 1

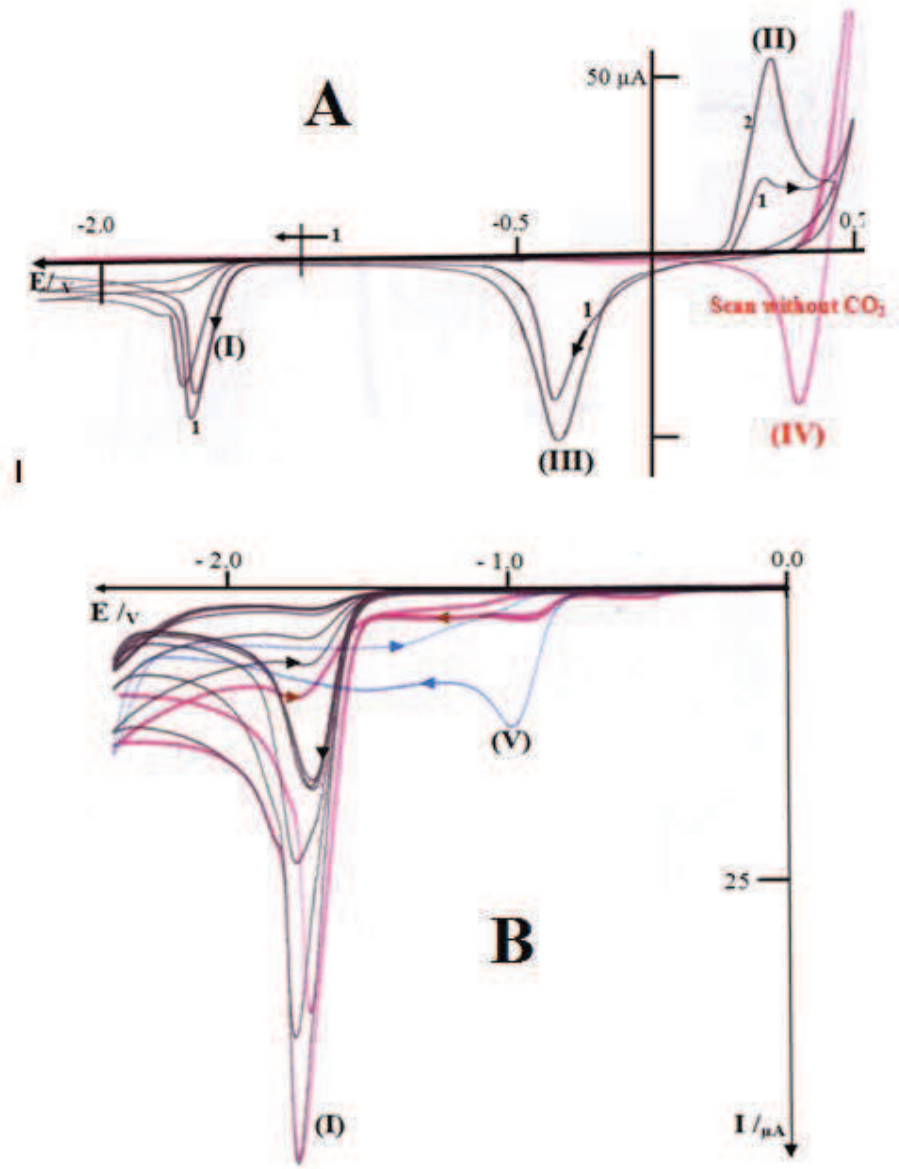
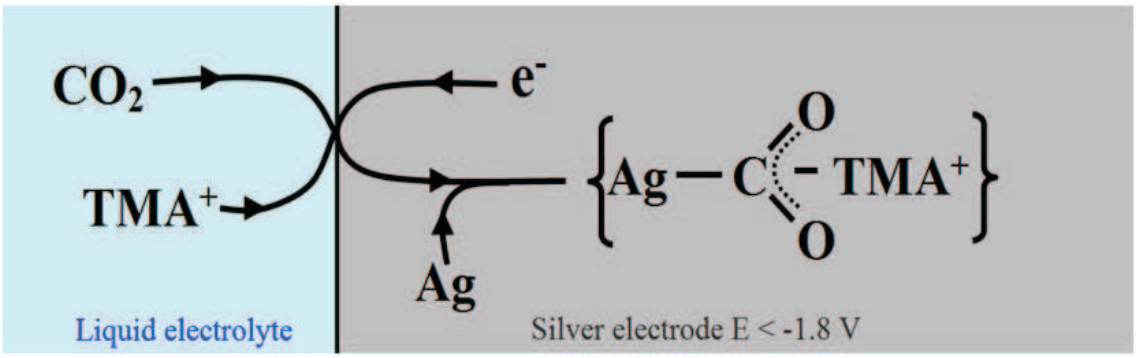


Figure 2



$$Ag + + CO_2 + M^+ + e^- \xrightarrow[\text{Step I}]{M^+ = (TMA^+)} \{Ag\text{-}CO_2\text{-}M\}_s \quad (1)$$

$$\{Ag\text{-}CO_2\text{-}M\}_s - e^- \xrightarrow{\text{Step II}} \{Ag\text{-}CO_2\text{-}M\}_s^+ \quad (2)$$

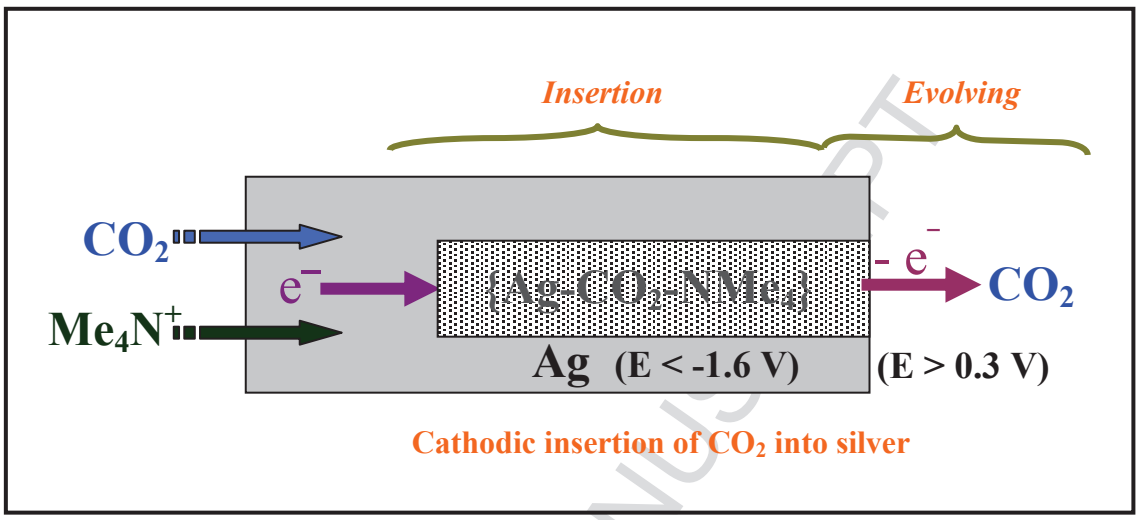
$$\{Ag\text{-}CO_2\text{-}M\}_s^+ \xrightarrow{\text{Scission}} Ag^+_s + (CO_2)_s + M^+_s \quad (3)$$

$$Ag_s^+ + e^- \xrightarrow{\text{Step III}} Ag^0 \quad (4)$$

$$(CO_2)_s + Ag^0 + M^+ + e^- \longrightarrow \{Ag\text{-}CO_2\text{-}M\}_s \quad (5)$$

$$\{Ag\text{-}CO_2\text{-}M\}_s + RI \xrightarrow{\text{E.T.}} R^{\bullet} + Ag^+_s + (CO_2)_s + M^+I^- \quad (6)$$

Scheme 1



Graphical Abstract

Highlights

Large electrochemical insertion of carbon dioxide in massive silver > Surfacial decoration versus mass modification > Ag-CO_2- electrolyte cation transient for a new solid material > Specific use of tetramethylammonium salts for a successful mass carboxylation > Stocking CO_2 with evolving under anodic electron transfer.